III.A.15 Reliable Seals for Solid Oxide Fuel Cells

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Objectives

- Develop sealing techniques for solid oxide fuel cells (SOFCs) that are reliable and cost-effective.
- Determine performance-limiting features of different sealing approaches.
- Determine seal degradation mechanisms.
- Optimize seal properties.

Approach

- Glass matrix composite seals can be engineered to provide a wide range of chemical and mechanical properties.
- Composite approach allows glass and filler to be optimized independently.
- Glass phase is above its glass transition temperature (Tg) at SOFC operating temperature to reduce thermal and mechanical strains.
- Viscosity, coefficient of thermal expansion (CTE), etc. can be controlled by adding unreactive powder.
- Volume fraction of glass phase can be reduced to minimum for seal, which reduces reactivity with fuel cell materials.

Accomplishments

- Developed and tested over 30 glass compositions with different glass transition temperatures and expansion coefficients.
- Made glass-ceramic powder composites by varying glass and additive compositions and volume fraction of powder additive; demonstrated that we can vary CTE in controlled manner.
- Sealed different composites to yttria-stabilized zirconia (YSZ) electrolytes; demonstrated good adhesion and mechanical strength.
- Showed composite seals are resistant to damage from thermal cycling.
- Made similar glass matrix composites, but with metal powder additives; sealed them to SOFC parts and showed that we can vary the seal properties in a systematic manner.
- Tested seals at 800-850°C for up to 200 hours; showed adhesion is maintained.

Future Directions

- Conduct more thermal cycling and long-time exposure tests at service temperature.
- Determine effects of environmental exposure; e.g., reducing and oxidizing atmospheres.
- Test new seal compositions and joining parameters.
- Develop pressure rupture test as a quick screen for seal compositions and processes.

- Perform more fundamental mechanical tests on composite seal materials at operating temperatures; e.g., flexural strength and fracture toughness.
- Determine seal adhesion to SOFC parts such as YSZ substrates.
- Investigate shaping and forming methods for composite seals such as tape casting and screen printing.

Introduction

Development of reliable methods for sealing solid oxide fuel cell stacks presents the most challenging set of performance criteria in the entire field of ceramic joining. For SOFC applications, the requirements on the sealing method include:

1. Adhesion of the sealing material to fuel cell components from room temperature to as high as 1000°C
2. Provide a leak-tight seal at the SOFC operating temperature
3. Ability to maintain a seal while accommodating strains from SOFC components with different CTEs
4. Lack of adverse reaction between the sealing material(s) and the fuel cell components
5. Chemical and physical stability of the sealant at temperatures up to 1000°C in oxidizing and reducing atmospheres
6. Thermal shock tolerance
7. Electrically insulating for some SOFC designs

All of the above properties must be maintained for SOFC operating lifetimes of up to 40,000 hours. The list is written in approximate order of decreasing stringency. That is, no matter what the SOFC design, the seal must be adherent and leak tight. On the other hand, some stack designs may require joining only similar materials and, thus, a matched CTE seal may be sufficient. Note also that the requirements may be contradictory. For example, being leak tight and adherent at high temperatures suggests a refractory, stiff sealant, which may work against the requirement for thermal strain accommodation. Such situations are common, and seal developers know that seal design is specific to a particular component geometry and usually requires compromises among competing requirements.

Approach

Under DOE sponsorship, this project is developing an approach to sealing SOFCs that can be tailored to the specific requirements of the vertical teams in the DOE / Solid State Energy Conversion Alliance (SECA) program. The technique combines extensive capabilities in composites and ceramic joining that have been developed at Sandia over the past 15-20 years. In our judgment, relief of thermal expansion mismatch stresses will require SOFC seals to incorporate either a ductile metal or a high-viscosity glass that can relieve stresses through viscous creep. Other design and operational constraints on SOFCs, which as discussed above frequently are in opposition, severely restrict the options for seal materials. Based on our prior experience in ceramic joining and on results obtained so far on this project, we believe we have greatest design flexibility using ceramic-filled glasses and metal-filled glass composites. We have demonstrated that we can control properties such as glass transition temperature and thermal expansion coefficient by varying the compositions, amounts, and microstructures of the different phases. Design choices are guided by thermochemical and composite microstructural models that allow us to target specific seal properties for a given design. Several seal systems are showing promise in functional tests. In future work we will use our extensive background in modeling composite properties to optimize the compositions and structures for specific combinations of seal properties for best performance.

The specific tasks for this project include the following:

1. Consult with vertical teams to learn their specific requirements.
2. Synthesize candidate glasses.
3. Measure glass properties such as Tg, CTE, and possibly viscosity as a function of temperature.
4. Choose ceramic powder filler, particle size, and particle morphology.

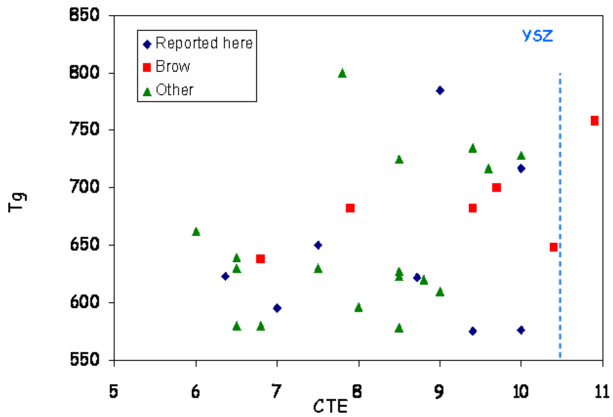

Figure 1. Glass Compositions Plotted as a Function of Glass Transition Temperature (Tg) and Coefficient of Thermal Expansion (CTE)

5. Design and make ceramic-filled glass composite sealants in a range of compositions and microstructures.
6. Make test seals with specified SOFC materials and measure strengths of bonded test specimens as a function of temperature.
7. Determine stability of seal over time at temperature by analyzing interfaces of specimens after long-term heating.
8. Measure deformation of candidate sealant-SOFC bilayers in situ as a function of temperature using an apparatus that is unique to Sandia.
9. Use measured properties (e.g., strains) as inputs to 3D finite element modeling computations to calculate stresses for different SOFC stack designs. Alternatively, we can provide the property data (e.g. strain vs. temperature data) to the vertical teams and they can do the computations themselves.
10. Apply property data, engineering data, and finite element simulations to design seals that minimize stresses (and to define practical limits for the stresses in SOFCs); transfer results to vertical teams as they are obtained.

Results

We have made over 30 different glass compositions with potential for the composite seal approach and measured their physical properties. Figure 1 shows the compositions on a plot of glass transition temperature (Tg) as a function of coefficient of thermal expansion (CTE). The plot shows that we have glasses with a wide range of properties available.

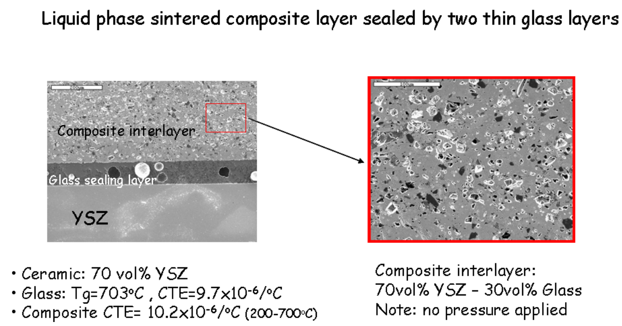

Figure 2. Glass-Ceramic Seal Bonded to YSZ Substrate with Thin Layer of the Same Glass as in the Composite

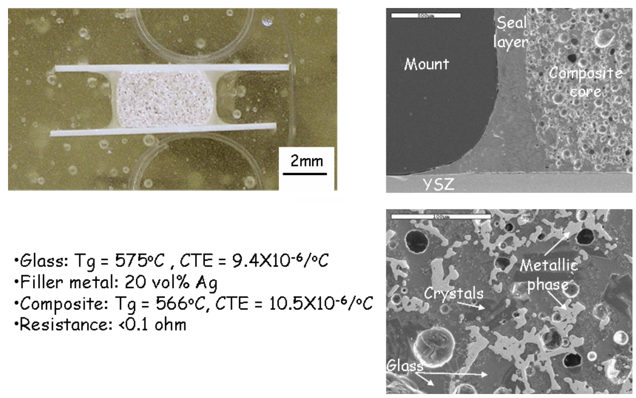

Figure 3. Micrographs of glass-Ag composite showing that an electrically conductive seal can be obtained by adjusting the amount of the Ag. If the volume fraction of Ag is reduced, an insulating seal results.

Figure 2 shows several micrographs of a seal to YSZ that comprises a composite layer with 70 vol% YSZ powder and 30 vol% of one of our sealing glasses bonded with a thin layer of the same glass. The composite CTE has been adjusted to 10.2 x 10^{-6}/°C. The seal adheres tightly to the YSZ and survived multiple thermal cycles up to 850°C.

Glass composite seals incorporating a ductile metal are particularly able to accommodate CTE mismatch stresses through deformation. Figure 3 is an example with 20 vol% Ag and the remainder one of our glasses. This composition is electrically

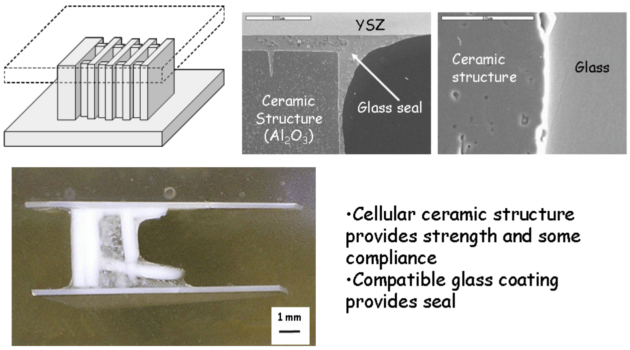

Figure 4. The Sandia-developed Robocasting technique, a type of freeform deposition, can make seals that combine ceramic and glass structures to optimize mechanical properties. In this example, a somewhat compliant cellular alumina structure provides mechanical support and the glass layer provides the seal.

Type of cast	Additive / vol%	Vol% Solid
Pure glass	N/A	65%
Glass-ceramic composite	14a / 30vol%	65%
Glass-metal composite	Ni / 30vol%	65%

Typical volume% solid of common tape cast is around 55-65%

Tape cast thicknesses 0.56 to 0.85mm (green)

Typically 0.5 to 1.5mm

Figure 5. Glass-powder composites can be prepared as green tapes similar to those used in microelectronic packaging. This approach allows more processing options.

conductive because the Ag is just above the percolation limit. We can obtain an insulating seal with almost the same mechanical properties by reducing slightly the amount of Ag.

We have used the Sandia-developed freeform fabrication technique known as Robocasting to make some demonstration seals. The idea is to show the range of ceramic-glass structures that are possible and that may be designed to optimize specific mechanical properties. In Figure 4, a cellular alumina structure provides mechanical support for the seal while the glass provides the hermetic seal to the YSZ. This seal proved particularly robust in thermal cycling tests.

Availability of manufacturing processes is always an issue in materials joining. Figure 5 illustrates some experiments that show that glass-ceramic composite seals can be formed using preforms that are tapecast using techniques common to microelectronic packaging. The green (unfired) tape can be cut to the shape required for the bond area and stacked so that the whole assembly is sealed and otherwise processed in a co-fire operation.

Conclusions

We have demonstrated the potential of the glass-powder composite approach for sealing SOFCs. We have shown that we can independently vary compositions and microstructures to achieve desired seal properties and that those properties can be targeted to seal different SOFC materials. We have demonstrated a number of techniques for applying the seals that would be practical in a manufacturing setting.